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THE PREPARATION AND PROPERTIES OF SOME IRIDIUM-SUBSTITUTED DIFLUOROPHOSPHINES: SYNTHESIS OF SOME PF_2-BRIDGED HETEROMETAL COMPLEXES *

E.A.V. EBSWORTH*, ROBERT O. GOULD, NEIL T. MCMANUS, DAVID W.H. RANKIN, MALCOLM D. WALKINSHAW and JOHN D. WHITELOCK

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ (Great Britain)

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Summary

Reaction between *trans*-$Ir(CO)X(PEt_3)_2$ and PF_2X ($X = Cl$) at 193 K gives $Ir(CO)X(PEt_3)_2PF_2X$, which rearranges at 298 K to form $Ir(CO)X_2(PEt_3)_2PF_2$ (Z). When X = Br or I, product Z is formed at room temperature, but only traces of the intermediate are detected when X = Br, and none at all when X = I. The end-products have been isolated and characterised by NMR and IR spectroscopy and by analysis, and by reactions with O_2, S_8, Se; with B_2H_6; with $[M(arene)Cl_2]_2$ (M = Ru or Os); and with $PtCl_2(COD)$. Reaction with H_2G (G = O, S, Se) gives $Ir(CO)X_2(PEt_3)_2P'FH(G)$. Crystal structures are reported for $Ir(CO)Cl_2(PEt_3)_2P'F_2O$, for $Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)RuCl_2$(*p*-cymene), and for $[Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)]_2PtCl_2$. In each molecule the angle IrP'Q (Q = O, Ru, Pt) is unusually wide.

Compounds of three-coordinated P in which one substituent is a transition metal are relatively unusual [1–4]. In reactions of PF_2X (X = Cl, Br or I) with $PtHX(PEt_3)_2$, we have obtained [5] binuclear complexes in which two Pt atoms are bridged by PF_2; the mechanism by which these are formed is not fully clear, but it seems possible that the initial step involved oxidative addition of P–X to the Pt centre, leading to the formation of a complex containing Pt–PF_2 which then reacted further at very low temperatures. We therefore investigated the reactions between PF_2X and iridium complexes of the form $Ir(CO)X(PEt_3)_2$, to see whether the greater relative stability of 6-coordinated iridium(III) would allow us to isolate and study Ir–PF_2 complexes. A preliminary account of this work has already appeared [6].

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983.

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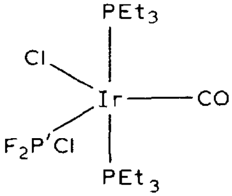
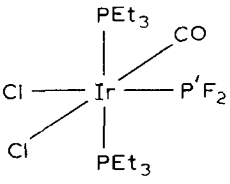
Results

(a) Synthesis of $Ir-PF_2$ complexes

Reaction between PF_2X and $Ir(CO)X(PEt_3)_2$ (X = Cl, Br, I). A solution of equimolar proportions of PF_2Cl and $Ir(CO)Cl(PEt_3)_2$ (I) in toluene at 193 K gave $^{31}P\text{-}\{^1H\}$ spectra containing two sets of resonances. One set, with $\delta(P)$ 97 ppm, showed a wide triplet pattern characteristic of a PF_2 group; the value of $^1J(PF)$, 1333 Hz, is consistent [7] with 4-coordinated P, and so is the value of $\delta(P)$. Each line showed a narrow triplet splitting. The other set of resonances, with $\delta(P)$ -6.9 ppm (characteristic of coordinated Et_3P groups) showed a doublet splitting equal to the narrower triplet coupling in the PF_2-resonance, and a further small triplet coupling that we assign to $^3J(PF)$. We formulate this species as a complex of 5-coordinated iridium(I), with PF_2Cl as the fifth ligand (**A**). We have no evidence as to the detailed stereochemistry of this complex, which may well be fluxional. The NMR parameters are given in Table 1.



(A)



(B)

When the solution was warmed to room temperature, the $^{31}P\text{-}\{^1H\}$ and ^{19}F spectra changed. All the resonances due to the original product disappeared. They were replaced by new resonances in which the multiplet patterns were the same as in the original spectrum, but the chemical shifts and coupling constants were very different. The PF_2 resonance shifted to 365 ppm, $\delta(F)$ shifted from around 0 to -68 ppm, and $^1J(PF)$ dropped to about 1100 Hz. The very high value of $\delta(P)$ is consistent [1] with our formulation of this complex as a derivative of 6-coordinated iridium(III)

TABLE 1

NMR PARAMETERS FOR $Ir(CO)Y(PEt_3)_2P'F_2X$

(Data recorded in toluene at 298 K. Chemical shifts given as positive to high frequency of 85% H_3PO_4 (for P), CCl_3F (for F), or Me_4Si (for H))

X	Y	$\delta(P)$ (ppm)	$\delta(P')$ (ppm)	$\delta(F)$ (ppm)	$^1J(P'F)$ (Hz)	$^2J(PP')$ (Hz)	$^3J(PF)$ (Hz)
H	Br [a]	-1.5	140	-60.3	1112	41	4.8
H	I [b]	-7.2	142	-60.8	1105	38	n.r. [c]
Cl	Cl	-6.9	97	4.9	1333	42	9
Cl	Br	0.1	103	3.7	1332	44	8.8
Br	Br	0.3	110	6.3	1341	45	n.r.

[a] $\delta(H)$ 8.8 ppm; $^1J(P'H)$ 416 Hz; $^2J(FH)$ 62 Hz; $^3J(PH)$ 6 Hz. [b] $\delta(H)$ 8.7 ppm; $^1J(P'H)$ 418 Hz; $^2J(FH)$ 62 Hz; $^3J(PH)$ n.r. [c] n.r. means not resolved.

TABLE 2

NMR PARAMETERS FOR $Ir(CO)XY(PEt_3)_2P'F_2$

(Measurements in toluene at 298 K. Chemical shifts given as positive to high frequency of 85% H_3PO_4 (for P), CCl_3F (for F), or Me_4Si (for H))

X	Y	δ(P) (ppm)	δ(P′) (ppm)	δ(F) (ppm)	^1J(P′F) (Hz)	^2J(PP′) (Hz)	^3J(PF) (Hz)
Cl	Cl	−9.3	364.8	−68.3	1105	9.2	11.6
Br	Cl	−13.2	362.1	−66.3	1111	8.6	11.6
I	Cl	−18.7	359.5	−65.0	1117	7.5	11.3
Br	Br	−18.1	363.1	−64.7	1108	8.6	11.1
Cl	Br	ca. −13.5 [a]	365.6	−66.7	1102	9.8	11.1
I	Br	−24.0	361.6	−63.3	1113	7.4	10.9
Br	I	−25.6	366.7	−62.4	1107	9.5	10.9
I	I	−31.9	364.8	−61.1	1112	8.3	10.6
H [b]	Br	−10.8	367.7	−61.5	1111	25.9	17.1
H [c]	I	−5.4	380.8	−62.4	1105	26.4	17.0

[a] This product was only formed in the presence of others, and the Et_3P resonance was not clearly resolved. [b] δ(H) −15.2 ppm; ^2J(P′H) 7.5 Hz; ^2J(PH) 10.0 Hz; ^3J(FH) 11.5 Hz; from δ(H), H is *trans* to I. [c] δ(H) −8.3 ppm; ^2J(P′H) 9.9 Hz; ^2J(PH) 16.0 Hz; ^3J(FH) 11.4 Hz; from δ(H), H is *trans* to CO.

containing PF_2 bound to the metal (**B**). The complex has been isolated by evaporation of the solvent and its constitution confirmed by analysis. The NMR parameters are given in Table 2.

Support for this formulation comes from studies of the reactions between PF_2Br and $Ir(CO)Br(PEt_3)_2$ (II) and between PF_2I and $Ir(CO)I(PEt_3)_2$ (III). For the bromides, weak signals were detected in the $^{31}P\text{-}\{^1H\}$ spectrum at 193 K that could be assigned to a product of type **A** (see Table 1); it is noteworthy that $\delta(PF_2)$ has changed by 13 ppm in comparison with the analogous chloride. Even at this temperature the main product was of type **B**, and when the tube was warmed all the peaks due to the initial product disappeared. For the iodide, the only product detected was of type **B**. The NMR parameters are given in Table 2: the constancy of δ(P′) strongly supports our formulation in which there is no halogen bound to the PF_2 group. All the products of type **B** have been isolated, and their compositions as determined by analysis support our formulation. So do the chemical reactions (see below).

Reactions of PF_2H with $Ir(CO)X(PEt_3)_2$ (X = Cl, Br, I). Reaction of PF_2H with III at 193 K in toluene gave one major product, whose $^{31}P\text{-}\{^1H\}$ spectrum consisted of two sets of resonances. The set at high frequency showed the wide triplet pattern characteristic of a PF_2 group; each line showed a narrow triplet coupling assigned to ^2J(PP′) and reflected in a doublet coupling in the other $^{31}P\text{-}\{^1H\}$ resonance, which is assigned to PEt_3 groups. The ^{19}F spectrum consisted of a doublet (^1J(PF)) of doublets (^2J(FH)). In the ^1H spectrum there were peaks due to Et_3P protons and a multiplet centred near δ 9 ppm. This showed a wide coupling (415 Hz) assigned to ^1J(P′H) for 4-coordinated P, with a smaller triplet coupling assigned to ^2J(FH) and equal to the smaller splitting in the ^{19}F spectrum. The values of δ(H) and ^1J(HP) establish that the proton is bound to the PF_2 group, and that the product is of type

A, with 5-coordinated iridium(I) bound to PF_2H. The NMR parameters are given in Table 1. When the solution was allowed to warm to room temperature, the signals due to the initial product disappeared. In the ^{31}P-{^{1}H} spectrum, the P′-resonance shifted from 140 ppm to 376 ppm, though still showing a narrow triplet coupling; when proton coupling was retained, an additional doublet splitting of around 10 Hz was resolved, so small as to show that there was no proton bound to the PF_2 group. The other P resonance shifted to somewhat lower frequency, though still appearing as a doublet (^{2}J(PP′)) of triplets (^{3}J(PF)). In the proton resonance spectrum, the multiplet at 9 ppm had disappeared, and a new and complex multiplet appeared at −15 ppm; this could be analysed as a doublet (^{2}J(HP)) of triplets (^{3}J(HF)) of triplets (^{3}J(HP′)). We therefore assign to this complex a structure of type **B**. From the value of the proton chemical shift, we suppose [8] that H is *trans* to halogen, and the couplings are consistent with this assumption. The NMR parameters are given in Table 2.

A similar reaction occurred between PF_2H and II. The only significant difference was that in the product of type **B** the chemical shift of the IrH proton was −8.5 ppm, a value [8] implying that H was *trans* to CO and not to halogen. The NMR parameters for the initial product are given in Table 1, and those for the eventual product of type **B** in Table 2. Reaction between PF_2H and I at 193 K gave traces of a product of type **A**. When the solution was allowed to warm to room temperature, the peaks due to this complex disappeared and no other product could be identified. None of the products was stable over an extended period at room temperature, and no attempt was made to isolate them. In the proton resonance spectrum of the reaction with III, however, resonances were observed that could be assigned to a particular additional species. At high frequency, a wide doublet (^{1}J(PH)) of triplets (^{2}J(HF)) of triplets (^{3}J(P′H)) was observed; the value of the chemical shift and of ^{1}J(PH) (see Table 3) showed that the complex concerned contained PF_2H as a ligand. In the low frequency region there was a doublet of triplets of doublets, of roughly the same intensity as the high frequency resonance. This multiplet is assigned to IrH; the values of its chemical shift (−9.0) and coupling constants imply [8] that H is *trans* to CO, and we deduce that the species is C, which is a cation. The only resonances we observed that could be assigned to an anion were those from PF_5H^-. This anion, a common by-product in reactions of PF_2H, is probably formed

TABLE 3

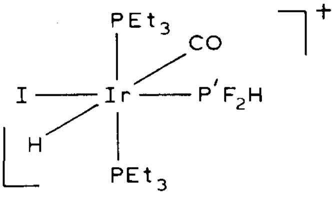
NMR PARAMETERS FOR $[Ir(CO)H'I(PEt_3)_2P'F_2H]^+$

(Data measured in toluene at room temperature. Shifts given as positive to high frequency of 85% H_3PO_4 (for P), CCl_3F (for F), and Me_4Si (for H))

δ(P)(ppm)	δ(P′)(ppm)	δ(F)(ppm)	δ(H)(ppm)	δ(H′)(ppm)
−26.0	122	−58.5	8.4	−9.0
^{1}J(P′F)(Hz)	^{1}J(P′H)(Hz)	^{2}J(FH)(Hz)	^{2}J(PP′)(Hz)	^{2}J(PH′)(Hz)
1095	529	70.2	19.5	10
^{2}J(P′H′)(Hz)	^{3}J(PH)(Hz)	^{3}J(FH′)(Hz)		
n.r. [a]	4	9		

[a] n.r. means not resolved.

through decomposition of PF_2H, giving (among other products) PF_3 and HF, which react together to give an acid that could have protonated the product of type **A** (at Ir) or **B** (at P). The NMR parameters are given in Table 3.



(C)

Reaction between PF_2X and $Ir(CO)Y(PEt_3)_2$ ($X \neq Y$). The only one of these reactions in which the initial formation of a complex of 5-coordinated iridium(I), type **A**, was observed was that between PF_2Cl and II; the NMR parameters of the complex are given in Table 1. The end-products of the reactions between all pairs of reagents were shown by elementary analysis to be equimolar adducts, and the NMR spectra showed them to be of type **B**, with terminal PF_2 groups. However, the precise products depended on the starting materials. Reaction between I and PF_2Br or PF_2I gave in each case a single product whose NMR parameters did not correspond with those of reactions between PF_2X and $Ir(CO)X(PEt_3)_2$. We conclude that the complexes formed are of the form $Ir(CO)ClX(PEt_3)_2P'F_2$ (X = Br or I), with two different halogens bound to iridium. In contrast to this, reaction between PF_2Cl and III gave four products. Two of them were identified from their NMR parameters as $Ir(CO)Cl_2(PEt_3)_2PF_2$ and $Ir(CO)I_2(PEt_3)_2PF_2$; a third was the same as the product of the reaction between PF_2I and I. We presume that the fourth also contains two different halogens bound to iridium, but in a different stereochemical relationship. Reactions between PF_2Cl and II, between PF_2Br and III, and between PF_2I and II each gave four analogous products.

It appears that in these systems, in contrast to the reactions between I and PF_2Br or PF_2I, the four products have been formed by halogen exchange:

$$PF_2X + Ir(CO)Y(PEt_3)_2 \rightleftharpoons PF_2Y + Ir(CO)X(PEt_3)_2$$

$$PF_2X + Ir(CO)X(PEt_3)_2 \rightarrow \underset{\textbf{(a)}}{Ir(CO)X_2(PEt_3)_2P'F_2}$$

$$PF_2X + Ir(CO)Y(PEt_3)_2 \rightarrow \underset{\textbf{(b)}}{Ir(CO)XY(PEt_3)_2P'F_2}$$

$$PF_2Y + Ir(CO)X(PEt_3)_2 \rightarrow \underset{\textbf{(c)}}{Ir(CO)YX(PEt_3)_2P'F_2}$$

$$PF_2Y + Ir(CO)Y(PEt_3)_2 \rightarrow \underset{\textbf{(d)}}{Ir(CO)Y_2(PEt_3)_2P'F_2}$$

While we do not know the stereochemical relationship between **b** and **c**, the compounds are clearly different; one of them, which we label **c**, was about twice as abundant as either **a** or **d** in each of the systems; **a** and **d** were formed in roughly comparable amounts, and **b** was present in substantially smaller proportions. The NMR parameters are collected in Table 2.

TABLE 4

NMR PARAMETERS FOR SOME DERIVATIVES OF $Ir(CO)X_2(PEt_3)_2P'F_2$ IN WHICH P' IS 4-COORDINATED

(Chemical shifts are given as positive to high frequency of 85% H_3PO_4 (for P), CCl_3F (for F), or Me_2Se (for Se))

Species	δ(P) (ppm)	δ(P') (ppm)	δ(F) (ppm)	$^1J(P'F)$ (Hz)	$^2J(PP')$ (Hz)	$^3J(PF)$ (Hz)	other
$Ir(CO)Cl_2(PEt_3)_2P'F_2BH_3$ [a]	−9.6	245	−57.6	1108	8.4	8.4	–
$Ir(CO)I_2(PEt_3)_2P'F_2BH_3$ [a]	−35.8	250	−46.9	1088	7.5	9.5	–
$Ir(CO)Cl_2(PEt_3)_2(P'F_2)RuCl_2(C_6H_6)$ [b]	−14	250.8	n.o.	1112	8	n.o.	–
$Ir(CO)Cl_2(PEt_3)_2(P'F_2)RuCl_2($*p*-cymene$)$ [b]	−13.8	252.6	−21.7	1109	7.6	7.6	–
$Ir(CO)Cl_2(PEt_3)_2(P'F_2)OsCl_2($*p*-cymene$)$ [b]	−13.9	192.6	−25.1	1075	8.3	8.3	–
$[Ir(CO)Cl_2(PEt_3)_2(P'F_2)]_2PtCl_2$ [c]	−11.2	177.2	−32.2	1111 [d]	9.4 [e]	n.o.	$^1J(PtP')$ 3360 Hz $^2J(PtF)$ 472 Hz
$Ir(CO)Cl_2(PEt_3)_2P'F_2O$ [a]	−9.0	7.4	−12.7	1201	20.3	3.0	–
$Ir(CO)Cl_2(PEt_3)_2P'F_2S$ [a]	−11.5	92.5	−2.3	1183	16.7	4.8	–
$Ir(CO)Cl_2(PEt_3)_2P'F_2Se$ [a]	−12.6	92.4	−2.5	1203	15.4	4.9	δ(Se) 208.7 ppm $^1J(PSe)$ 870 Hz $^2J(FSe)$ 83.6 Hz

[a] In toluene. [b] In nitromethane. [c] In dichloromethane. [d] Separation between strongest lines in P' spectrum, which in this spin system is $|^1J(P'F)+{}^3J(P'F)|$. [e] Separation between strongest lines in complex P resonance.

B. Reactions of complexes containing Ir–PF_2 groups

(a) Reaction of $Ir(CO)X_2(PEt_3)_2P'F_2$ *(X = Cl, Br or I) with* B_2H_6

The NMR spectra of 1/2 (B_2H_6/Ir) solutions of the reagents in CH_2Cl_2 at room temperature were markedly different from those of the starting materials, and showed that reaction had occurred to give $Ir(CO)X_2(PEt_3)_2P'F_2BH_3$. The $P'F_2$ ^{31}P resonances were shifted from their positions in the spectra of the starting materials by about 100 ppm to low frequency, and the lines were very broad (probably because of unresolved P–B coupling). In the ^{19}F spectra, the resonances appeared as wide doublets ($^1J(P'F)$) of triplets ($^3J(FP)$) of quartets (assigned to $^3J(FPBH)$). The NMR parameters are given in Table 4. The product with X = I was isolated as a pale yellow solid and analysed; the composition agreed with the proposed formulation, and the infrared spectrum contained bands assigned to ν(BH) and ν(BP).

(b) Reaction of $Ir(CO)Cl_2(PEt_3)_2P'F_2$ *(Z) with Group VI elements*

Reactions between Z and O_2, S_8 or red Se were allowed to occur in CH_2Cl_2 at room temperature. The products were identified by their NMR and infrared spectra and (Q = S) by analysis as $Ir(CO)Cl_2(PEt_3)_2P'F_2Q$ (Q = O, S, Se). The ^{77}Se spectrum of the selenide, a wide doublet of triplets, confirms this formulation; the crystal structure of $Ir(CO)Cl_2(PEt_3)_2P'F_2O$ was determined, and corroborates our conclusions. The structural parameters are described and discussed below, in the structural section; NMR parameters are given in Table 4.

TABLE 5

NMR PARAMETERS FOR $Ir(CO)Cl_2(PEt_3)_2P'FH(G)$ (G = O, S, Se)

(Measurements were made for solutions in toluene at room temperature. Chemical shifts were taken as positive to high frequency of 85% H_3PO_4 (for P), CCl_3F (for F), Me_4Si (for H), and Me_2Se (for Se): n.r. means not resolved.)

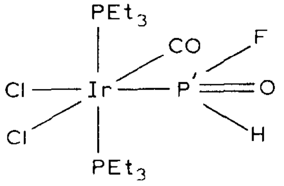
Parameter	G		
	O	S	Se[a]
$\delta(P_a)$ (ppm)	−8.8	−9.0	−10.0
$\delta(P_b)$ (ppm)		−16.6	−18.5
$\delta(P')$ (ppm)	46.9	79.6	82.2
$\delta(F)$ (ppm)	−42.2	−73.3	−93.5
$\delta(H)$ (ppm)	8.2	8.4	8.0
$^1J(P'F)$ (Hz)	1004	1001	1011
$^1J(P'H)$ (Hz)	530	507	492
$^2J(P_aP_b)$ (Hz)	-	321.2	322.3
$^2J(P_aP')$ (Hz)	15.2	14	14
$^2J(P_bP')$ (Hz)		12	11
$^2J(HF)$ (Hz)	76.6	75.1	72.9
$^3J(P_aF)$ (Hz)	5.4	12	12
$^3J(P_bF)$ (Hz)		1	1
$^3J(P_aH)$ (Hz)[b]	2.8	7.1	6.9
$^3J(P_bH)$ (Hz)[b]		n.r.	n.r.

[a] δ(Se) 161.9 ppm; $^1J(PSe)$ 735 Hz; $^2J(FSe)$ 25 Hz. [b] We could not tell whether the coupling resolved was to P_a or P_b; the designation was arbitrary.

Reaction of Z with $MCl_2(COD)$ (M = Pd, Pt). Reaction between Z and $PtCl_2(COD)$ in molar ratio (Z/Pt) of just below 2/1 in CH_2Cl_2 gave a white crystalline solid after solvent and volatile material had been removed. The solid was shown by analysis, by X-ray crystallography and by NMR spectroscopy to be *cis*-$[Ir(CO)Cl_2(PEt_3)\text{-}\mu\text{-}(P'F_2)]_2PtCl_2$. The NMR parameters are given in Table 4, the crystallographic data are presented and discussed in the structural section below, and analytical data are given in the experimental section. Because the ^{19}F and ^{31}P spectra comprise a complex spin system, and because the spectra are not fully resolved, we could not determine all the parameters accurately. Reaction between Z and $PdCl_2(COD)$ gave a mixture of products which could neither be identified from their NMR spectra nor separated from one another.

Reaction of Z with $[\eta^6\text{-(arene)}M'Cl_2]_2$ where M' = Ru or Os, and arene = benzene or p-cymene. Reaction between Z and $[\eta^6\text{-(}p\text{-cymene)}RuCl_2]_2$ in toluene (18 h) at room temperature gave an orange precipitate whose NMR spectra in nitromethane showed it to be a single compound; it was shown by analysis and by X-ray crystallography to be $Ir(CO)Cl_2(PEt_3)_2\text{-}\mu\text{-}(P'F_2)RuCl_2(p\text{-cymene})$. An analogous product was formed under the same conditions from Z and $[\eta^6\text{-(}p\text{-cymene)}OsCl_2]_2$. This compound was characterised by NMR and mass spectrometry. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the product of reaction between Z and $[\eta^6\text{-}(C_6H_6)RuCl_2]_2$ was similar to those of the other products, but this compound decomposed in solution and was not isolated. The NMR parameters for all these compounds are given in Table 4, and the structure of the Ru-*p*-cymene complex is described and discussed in the structural section below.

Reactions of Z with H_2G (G = O, S, Se). These reactions all gave a single main product, with a number of other unidentified species in much smaller concentrations. The reaction between Z and H_2O in CH_2Cl_2 gave a main product whose $^{31}P\text{-}\{^1H\}$ NMR spectrum consisted of two signals. That at high frequency appeared as a doublet ($^1J(P'F)$) of triplets ($^3J(PF)$). In the ^1H spectrum, besides the complex multiplet due to Et_3P protons, there was a resonance at high frequency that appeared as a doublet ($^1J(P'H)$) of doublets ($^2J(FH)$) of triplets ($^3J(PH)$), though under line narrowing the apparent triplet patterns appeared as doublets of doublets, suggesting slightly different values of $^3J(PH)$ to the two Et_3P phosphorus nuclei. We interpret these results as showing that there has been part-hydrolysis of the $P'F_2$ group to give complex **D** with a PFH(O) ligand.



(D)

Since P' is chiral, the two Et_3P phosphorus nuclei are in principle non-equivalent; the $^{31}P\text{-}\{^1H\}$ spectrum at 25 MHz showed no sign of this non-equivalence, and the only suggestion of it that we detected was in the slight deviation of the P'H proton resonance from the ideal triplet pattern.

Reaction between Z and H_2S was slower, and the NMR tube had to be warmed to 313 K to encourage the process to completion; reaction with H_2Se was complete in 2 h at 298 K. The ^1H and ^{31}P NMR spectra of the main products were qualitatively similar. The P′ resonances appeared as wide doublets ($^1J(P'F)$) of triplets ($^2J(PP')$), which showed additional doublet couplings of 500 Hz ($^1J(PH)$) when proton coupling was retained. We deduce that complexes analogous to **D** have been formed, but with S or Se in place of O. This was confirmed for the selenide by the $^{77}Se\text{-}\{^1H\}$ spectrum, which appeared as a doublet ($^1J(P'Se)$) of triplets ($^3J(SeP)$). Here too the ligand PFH(G) is chiral, and so the Et_3P resonance pattern in the P-{H} spectrum should be the AB part of an ABMX spin system. We were able to interpret the P-{H} resonances in these terms. The ^{19}F spectra, doublets of doublets of doublets, confirmed our interpretation. The P′H proton resonance spectra also appeared as a doublet of doublets of doublets. It is clear that the non-equivalence of the two Et_3P nuclei is more marked when G = S or Se than when G = O, a reasonable observation in view of the greater similarity of F and O as substituents at P′ than of F and S or F and Se. The NMR parameters for these species are given in Table 5.

Discussion

The reaction of PF_2X with $Ir(CO)X(PEt_3)_2$ proceeds initially through coordination of PF_2X to the metal, and then by oxidative addition of P–X to Ir, forming a

The reaction of PF_2X with $Ir(CO)X(PEt_3)_2$ proceeds initially through coordination of PF_3X to the metal, and then by oxidative addition of P–X to Ir, forming a derivative of iridium(III) with PF_2 bound to the metal. Though we have not been able to determine the crystal structure of any of the compounds of type **B**, the evidence from NMR parameters and from chemical reactions leaves no room for doubt: the unusual chemical shift of the PF_2 phosphorus nucleus, which is almost independent of X, is entirely consistent with our formulation, and is also in keeping with chemical shifts in the metal complexes containing PX_2 ligands; the reaction of the products with B_2H_6 and with the complexes of Pt, Ru and Os, show that the $P'F_2$ phosphorus atom has a lone pair of electrons. In the preparative reaction between PF_2X and $Ir(CO)Y(PEt_3)_2$ at low temperatures, oxidative addition is faster than halogen exchange when Y is Cl and X is Br or I, but slower in all other cases; this implies that the rate of oxidative addition depends more on the P–X bond than the rate of halogen exchange does. The observation is a little surprising in view of the softness of iridium(I). It also follows that halogen exchange in the 6-coordinate iridium(III) complexes is slow at room temperature.

It is easy to oxidise the PF_2 ligand with O, S or Se, as has been found in related species; reaction with H_2O, H_2S and H_2Se leads to the formation of some complexes containing unusual P ligands and in each case only one fluorine atom is displaced under our experimental conditions. The most important reactions are those with complexes of other platinum metals containing ligands that are easily displaced. These show that compounds containing $M\text{–}P'F_2$ groups behave as phosphines, and so can be used to synthesize mixed-metal complexes. In reactions between PF_2X and 4-coordinated complexes of platinum(II), the products isolated at room temperature contain binuclear species with $Pt\text{–}PF_2\text{–}Pt$ bridges [5]; our results show that $P'F_2$ bound to 6-coordinated iridium(III) is not sufficiently nucleophilic to displace Cl^- from another molecule to form a bridged cation.

NMR parameters

In complexes of type **A**, the NMR parameters are fairly characteristic. The chemical shift of PF_2X depends on X; when X is halogen, $\delta(F)$ is around 0, and $\delta(P')$ is around +100 ppm. In each compound $^2J(PP')$ is about 40 Hz, whereas $^3J(PF)$ is less than 10 Hz and is not always resolved. In all the complexes containing PF_2–M groups, $\delta(P')$ is around +360 ppm, and varies little with X; $\delta(F)$ is around −60 ppm, and the total spread of values is less than 7 ppm. $^1J(PF)$ is in the range 1110 ± 10 Hz, and (except with IrH ligands) $^2J(PP')$ is 8.5 ± 2 Hz and $^3J(PF)$ is 11.0 ± 0.05 Hz. With IrH ligands, $^2J(PP')$ goes up to ca. 25 Hz and $^3J(PF)$ to 17 Hz, even though from chemical shifts it appears that the two complexes in question have different stereochemistries; these observations imply that the two- and three-bond couplings involved depend on the electron density at Ir. When the lone pair of electrons at PF_2 is involved in bonds either through donation or oxidation, $\delta(P')$ drops, $\delta(F)$ increases, $^1J(PF)$ increases, $^2J(PP')$ increases and $^3J(PF)$ drops. These changes are greatest on formal oxidation. In the ^{31}P spectrum of the products of reaction with H_2Y, the chirality of the ligands allowed us to measure $^2J(PP_{trans})$. When Y = S or Se, these couplings were large, as expected (ca. 320 Hz).

Description of structures

Crystal data for $Ir(CO)Cl_2(PEt_3)_2P'F_2O$ (**1**), $Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)RuCl_2$(*p*-cymene) (**2**) and $[Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)]_2PtCl_2$ (**3**) are given in Table 6. Selected bond lengths and angles are given in Tables 7 and 8 and perspective views of the structures are given in Fig. 1–3. There is a significant difference in all structures between the Ir–Cl (*trans* to CO) and Ir–Cl′ (*trans* to PF_2) bond lengths, which have weighted means of 2.368(6) and 2.432(8) Å, respectively. Similarly, the weighted mean lengths of Ir–PEt_3 (*trans* to PEt_3) and Ir–$P'F_2$ (*trans* to Cl) are 2.409(8) and 2.267(9) Å respectively. The angles at Ir show a considerable distortion from octahedral symmetry, shown particularly in the *trans* P–Ir–P angles.

(Continued on p. 239)

TABLE 6

CRYSTAL DATA FOR $Ir(CO)Cl_2(PEt_3)_2P'F_2O$ (**1**), $Ir(CO)Cl_2(PEt_3)_2(P'F_2)RuCl''_2$(*p*-cymene) (**2**), AND $[Ir(CO)Cl_2(PEt_3)_2(P'F_2)_2]PtCl''_2$ (**3**)

	1	**2**	**3**
a (Å)	15.446(10)	12.960(16)	15.081(12)
b (Å)	9.160(8)	13.673(7)	10.665(10)
c (Å)	14.940(10)	18.487(18)	30.485(20)
β (°)	95.19(5)	95.64(6)	112.08(5)
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
M	612.4	902.6	1458.8
Z	4	4	4
d_c (g cm^{-3})	1.93	1.84	2.13
μ(Mo-K_α) (cm^{-1})	72.0	52.6	100.1
U (Å^3)	2108	3260	4544
Data used ($F > 5\sigma(F)$)	2517	2170	3274
final *R*	0.070	0.075	0.089
final R_w	0.079	0.094	0.109

TABLE 7

BOND LENGTHS (Å) IN **1**, **2**, AND **3** FOR THE METAL COORDINATION SPHERES

Bond	**1**	**2**	**3a**		**3b**
Ir–Cl	2.370(6)	2.379(9)	2.345(14)		2.351(14)
Ir–Cl′	2.415(6)	2.458(10)	2.459(16)		2.457(17)
Ir–P′	2.252(6)	2.278(8)	2.289(15)		2.296(15)
Ir–P	2.406(6)	2.418(8)	2.423(14)		2.456(14)
	2.397(5)	2.413(9)	2.414(17)		2.431(15)
Ir–C	1.943(21)	1.83(3)	1.92(7)		1.62(6) [a]
C–O	1.00(3)	1.12(4)	1.02(8)		1.33(8) [a]
P–F	1.564(16)	1.583(17)	1.52(3)		1.52(3)
	1.534(16)	1.591(18)	1.51(3)		1.62(4)
P–X [b]	1.449(19)	2.289(8)	2.243(15)		2.214(15)
X–Cl″		2.405(8)		2.333(16)	
		2.396(9)		2.363(16)	

[a] The position of this carbon atom is not properly defined. [b] X is O in **1**, Ru in **2** and Pt in **3**.

TABLE 8

SELECTED ANGLES (°) IN **1**, **2**, AND **3** FOR THE METAL COORDINATION SPHERES

Angle	**1**	**2**	**3a**		**3b**
P–Ir–P	171.2(2)	167.3(3)	166.9(5)		169.4(5)
P′–Ir–Cl	175.9(2)	176.9(3)	175.8(5)		171.7(6)
C–Ir–Cl	178.7(6)	176.1(11)	173.6(20)		176.5(23)
P–Ir–Cl	89.6(2)	86.6(3)	87.7(5)		85.4(5)
	91.1(2)	90.9(3)	85.4(5)		85.4(5)
P–Ir–Cl′	83.3(2)	85.1(3)	82.8(6)		87.2(5)
	87.9(2)	82.4(3)	86.6(5)		87.4(5)
P′–Ir–P	96.9(2)	97.5(3)	96.5(5)		96.3(5)
	91.9(2)	94.9(3)	94.4(6)		90.2(5)
P–Ir–C	91.3(6)	91.0(11)	94.8(20)		93.8(23)
	88.1(6)	90.7(11)	91.0(20)		95.1(23)
P′–Ir–Cl	86.3(2)	87.9(3)	88.8(5)		97.8(5)
P′–Ir–C	92.7(6)	95.5(11)	96.7(20)		85.6(23)
Cl–Ir–Cl′	89.6(2)	90.5(3)	94.1(5)		89.9(5)
C–Ir–Cl′	91.3(6)	86.2(11)	80.2(20)		86.7(23)
Ir–C–O	175.5(21)	171(3)	179(6)		165(5) [a]
Ir–P′–F	108.6(6)	105.7(7)	111.6(13)		104.7(14)
	110.5(6)	108.7(7)	108.5(13)		106.4(14)
Ir–P–X [b]	119.8(8)	132.3(3)	120.4(7)		126.7(7)
F–P–F	96.3(8)	93.0(9)	94.9(17)		99.1(18)
F–P–X [b]	110.1(10)	106.5(7)	107.0(13)		107.9(14)
	109.0(10)	103.7(7)	111.5(14)		108.5(14)
P′–X–Cl″		85.2(3)	84.7(6)		83.5(5)
		89.6(3)	173.8(5)		172.6(6)
Cl″–X–Cl″		88.8(3)		90.1(6)	
P′–X–P′				101.9(5)	

[a] The position of this carbon atom is not properly defined. [b] X is O in **1**, Ru in **2** and Pt in **3**.

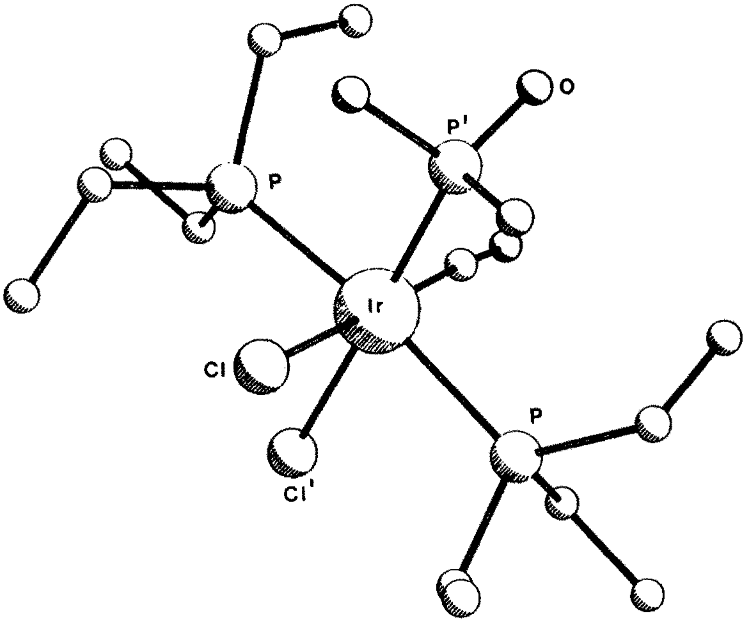


Fig. 1. Perspective view of $Ir(CO)Cl_2(PEt_3)_2PF_2O$.

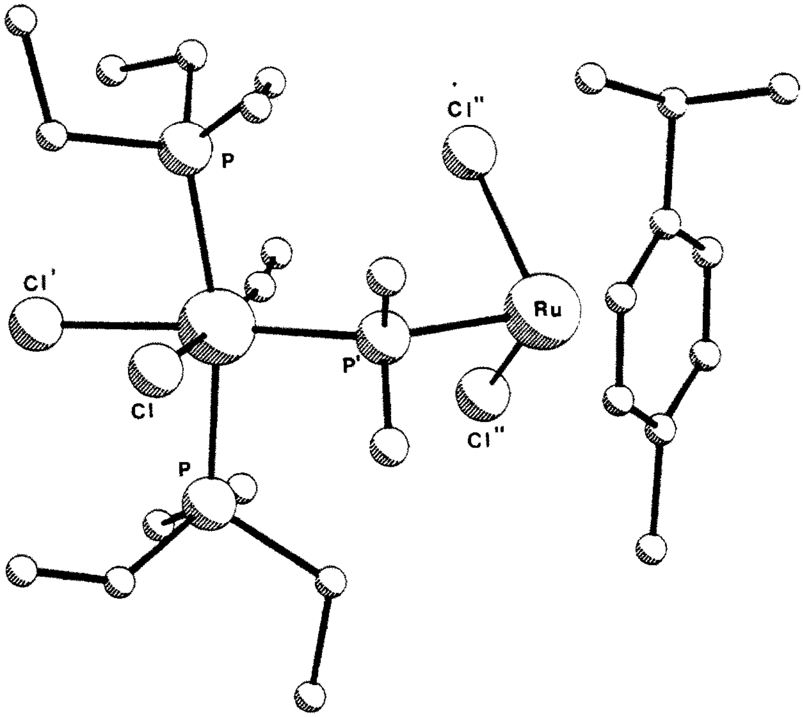


Fig. 2. Perspective view of $Ir(CO)Cl_2(PEt_3)_2(PF_2)RuCl_2$(*p*-cymene).

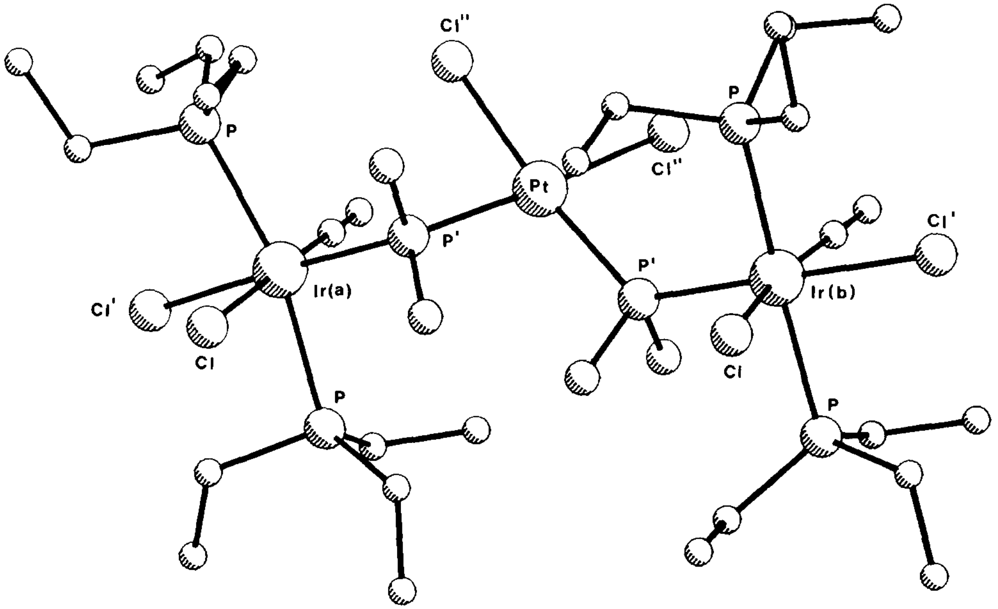


Fig. 3. Perspective view of $[Ir(CO)Cl_2(PEt_3)_2(PF_2)]_2PtCl_2$.

The Ir–P–X angles are generally large, particularly in compound **2**, suggesting that the ruthenium with a *p*-cymene moiety has a much greater steric effect than do the other phosphorus substituents. The angle is also unusually large for one of the iridium groups in compound **3**. In this case, the conformation is such that the P–F bonds almost eclipse Ir–P and Ir–Cl bonds, and the phosphorus and chlorine atoms are both bent away from the difluorophosphino group.

The F–P–F angles are similar to those in PF_3 [9], and the other angles at phosphorus are all fairly close to the tetrahedral angle.

Experimental

Volatile compounds were handled in conventional vacuum systems fitted with greased glass or with greaseless Sovirel taps, and involatile and air-sensitive materials using a Schlenk line and a Vacuum Atmospheres glove-box under dry nitrogen. Iridium starting materials were prepared as described elsewhere [10]; fluorophosphine derivatives [11] and the platinum [12], ruthenium and osmium [13] starting materials were made by published methods. The NMR spectra were recorded using JEOL FX60Q (^{31}P), Varian XL 100 (^{31}P, ^{19}F), and Bruker WH360 (^{1}H, ^{31}P, ^{77}Se) spectrometers, all operating in the FT mode. Infrared spectra were recorded using Perkin–Elmer 457 (4000–250 cm^{-1}) or 577 (4000–250 cm^{-1}) spectrometers, and microanalyses by means of a Perkin–Elmer 240 elemental analyser. The mass spectrum was recorded by courtesy of Kratos Ltd. using a Kratos-80RF spectrometer with fast atom bombardment.

The analytical data obtained are given in Table 9 and infrared spectral data in Table 10.

Reactions between iridium complexes and volatile materials were allowed to take place in NMR tubes using standard procedures. The metal complex (ca. 0.1 mmol) was weighed into an NMR tube, the appropriate solvent (ca. 3 ml) distilled in, and the volatile reagent allowed to condense in the tube, which was then sealed and studied at the chosen temperature.

Isolation of $Ir(CO)X_2(PEt_3)_2P'F_2$ and its derivatives

The sealed NMR tube in which the complex had been found was opened under N_2 and the volatile material removed on a Schlenk line. The resulting gum was triturated with petroleum ether (40–60°C) to give a powdery solid product, which was only obtained from pure starting-materials.

$Ir(CO)I_2(PEt_3)_2P'F_2BH_3$ was isolated as described above from an NMR tube in which $Ir(CO)I_2(PEt_3)_2PF_2$ had been allowed to react with B_2H_6 as described above.

$Ir(CO)Cl_2(PEt_3)_2P'F_2S$ and $Ir(CO)Cl_2(PEt_3)_2PF_2Se$ were isolated from reactions between Z and S or Se in a mixture of dry toluene and CS_2 after stirring under dry N_2 (15 h). Solvent was removed, toluene (2 ml) added, residual S or Se filtered off, and the solution was concentrated by evaporation. Precipitation by petroleum ether (40–60°C) yielded the products.

$Ir(CO)Cl_2(PEt_3)_2P'F_2O$ was obtained from a solution of Z in dichloromethane after exposing the solution to air (one week), evaporating solvent, redissolving the solid in the minimum of CH_2Cl_2 and adding petroleum ether (40–60°C).

$Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)MCl_2$(*p*-cymene) (M = Ru, Os) was obtained by adding $[MCl_2(arene)]_2$ (0.1 mmol) to a solution of Z (0.2 mmol) in dry degassed toluene, and storing the resulting slurry at room temperature (18 h). The precipitate (orange-

TABLE 9

ANALYTICAL DATA FOR COMPLEXES ISOLATED IN THIS WORK

Complex	Found (calcd.)(%)	
	C	H
$Ir(CO)Cl_2(PEt_3)_2PF_2$	26.2	5.2
	(26.2)	(5.1)
$Ir(CO)Br_2(PEt_3)_2PF_2$	23.0	4.6
	(22.8)	(4.4)
$Ir(CO)I_2(PEt_3)_2PF_2$	20.3	4.0
	(20.0)	(3.9)
$Ir(CO)BrCl(PEt_3)_2PF_2$	24.6	4.6
	(24.4)	(4.7)
$Ir(CO)ClI(PEt_3)_2PF_2$	22.6	4.3
	(22.7)	(4.4)
$Ir(CO)I_2(PEt_3)_2PF_2BH_3$	20.3	4.1
	(19.7)	(4.2)
$Ir(CO)Cl_2(PEt_3)_2PF_2S$	25.1	4.8
	(25.1)	(4.8)
$Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)RuCl_2$(*p*-cymene)	30.4	5.0
	(30.6)	(4.9)
$Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)OsCl_2$(*p*-cymene)	27.9	4.6
	(27.8)	(4.4)
$[Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)]_2PtCl_2$	21.7	4.6
	(21.4)	(4.1)

TABLE 10

INFRARED SPECTRA OF COMPLEXES ISOLATED IN THIS WORK (values in cm^{-1}) [a]

$Ir(CO)Cl_2(PEt_3)_2PF_2$	2042vs, 1260m, 1200m, 1035vs, 760vsb, 732vs, 625w, 575s, 420m, 388m, 310m.
$Ir(CO)Br_2(PEt_3)_2PF_2$	2042vs, 1261m, 1200s, 1035s, 760s, 745m, 560m, 440m, 380w.
$Ir(CO)I_2(PEt_3)_2PF_2$	2040vs, 1260m, 1200m, 1034s, 740m, 720s, 550m, 540m, 480w.
$Ir(CO)BrCl(PEt_3)_2PF_2$	2042m, 1255m, 1240w, 1198w, 1035s, 770m, 745s, 715s, 620w, 570m, 430w, 420m, 380m, 315w.
$Ir(CO)ClI(PEt_3)_2PF_2$	2040vs, 1260m, 1200m, 1034s, 750s, 730m, 615w, 570m, 560w, 530m, 430bw, 380w, 305w.
$Ir(CO)I_2(PEt_3)_2PF_2BH_3$	2410m, 2393m, 2345m, 2065vs, 2055vs, 1260m, 1240w, 1120m, 1055s, 1035vs, 840s, 820s, 805vs, 780s, 740s, 708s, 620m, 542m, 528m, 420m, 380m.
$Ir(CO)Cl_2(PEt_3)_2PF_2S$	2060s, 1260m, 1238w, 1030s, 820s, 800vs, 760s, 740s, 730s, 716s, 680s, 620w, 560m, 549m, 505w, 453m, 410w, 395w, 380m, 320w, 300vw, 280m.
$Ir(CO)Cl_2(PEt_3)_2PF_2Se$	2063s, 1244w, 1240w, 1215w, 1030s, 810s, 759s, 740s, 730s, 620w, 580s, 560m, 540m, 500w, 433w, 410w, 385w, 322w, 300w, 280m.
$Ir(CO)Cl_2(PEt_3)_2$-μ-$(PF_2)RuCl_2(C_6H_6)$	2055vs, 1265w, 1250w, 1150m, 1035s, 820m, 810s, 800s, 778s, 750m, 722s, 555s, 475m, 455m, 430w, 305w, 275w.
$Ir(CO)Cl_2(PEt_3)_2$-μ-$(PF_2)RuCl_2$(*p*-cymene)	2063vs, 1270w, 1034s, 800s, 765s, 755sh, 722s, 550m, 465m, 320w, 300w, 260w, 249w.
$Ir(CO)Cl_2(PEt_3)_2$-μ-$(PF_2)OsCl_2$(*p*-cymene)	2063vs, 1325w, 1267m, 1158w, 1115w, 1090w, 1035s, 910w, 878w, 802vs, 768vs, 725vs, 692w, 620w, 555s, 500m, 473s, 445sh, 418w, 341w, 320w, 310w, 265w.
$[Ir(CO)Cl_2(PEt_3)_2$-μ-$(PF_2)]_2PtCl_2$	2045vs, 2005w, 1258m, 1080bw, 1025s, 840s, 785s, 755s, 715s, 555m, 535m, 465s, 405w, 380w, 315w, 295w, 275w.

[a] s = strong; w = weak; m = medium intensity; v = very; b = broad; sh = shoulder.

red when M = Ru, yellow when M = Os) was filtered under dry N_2, was washed with degassed toluene and petroleum ether (40–60°C) and recrystallised from nitromethane.

$[Ir(CO)Cl_2(PEt_3)_2$-μ-$(PF_2)]_2PtCl_2$ was obtained by adding $PtCl_2$(COD) (0.1 mmol) to a solution of Z (0.18 mmol) in CH_2Cl_2. After shaking (5 min), volatile materials were removed, the residue redissolved and filtered, solvent once more evaporated and the product recrystallised from CH_2Cl_2/Et_2O.

Mass spectrum of $Ir(CO)Cl_2(PEt_3)_2$-μ-$(P'F_2)OsCl_2$*(p-cymene)*

The mass spectrum of this compound contained a molecular ion peak at *m/e* 992 ($Ir(CO)Cl_2(PEt_3)_2PF_2OsCl_2$(*p*-cymene) requires 992). Other prominent peaks were observed at *m/e* 973 (992 – F), 957 (992 – Cl), 858 (992 – *p*-cymene), and 561 $[Ir(CO)Cl(PEt_3)_2PF_2]$. Peaks at *m/e* 733 $[IrOs(PEt_3)_2$(*p*-cymene)Cl] and 453 $[IrOsCl_2]$ can only be understood if rearrangement has occurred in the spectrometer.

Structure determinations

Crystals of approximate cross section 0.2–0.4 mm were selected or cut from larger crystals, which were clear and colourless for all three compounds. Data were recorded to $2\theta_{max} = 45°$ using graphite monochromatised Mo-K_α radiation (λ 0.71072 Å) on a Nonius CAD-4 diffractometer (**2**) or a Stoe Stadi-2 diffractometer (**1** and **3**). The positions of Ir, Pt, and Ru atoms were determined from Patterson syntheses, and all other non-hydrogen atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were not located or included in any refinements. Anisotropic thermal parameters were refined for P, Cl, Ir, Pt and Ru; C, O, and F atoms were refined isotropically. In **1** and **3** the carbon atoms of ethyl groups were restrained to give aliphatic C–C 1.54 Å and P–C 1.84 and the phenyl ring of **1** was restrained to be regular with C–C 1.40 Å. In the final cycle of least squares (unit weights) the largest shift was less than 0.3 times the estimated standard deviation and difference Fourier syntheses showed no peaks higher than 1 eÅ^{-3} except in the immediate vicinity of Ir or Pt atoms. The refinements were carried out using the SHELX program [14]. Full lists of atomic parameters, bond lengths and angles, and tables of structure factors for **1**, **2** and **3** are available from the authors.

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